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TECHNOLOGY IN ACTION

CONTAINMENT OF RADIUM IN TAILING DUMPS

AS RADIUM ARSENATE

Final Report

by

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SUMMARY

Barium arsenate has been suggested as a reagent to control the release of radium, thorium and lead from uranium mill tailings, into the ground waters. This investigation shows that the optimum molar ratio of barium to arsenate is two to two or greater. In this range the radium concentration is kept below three pCi/L at a pH of six.

Canada has extremes in temperature and rainfall, hence chemical barriers must withstand these variations. Freeze-thaw and wet-dry cycling of barium arsenate barriers is shown to be non deleterious to their activity. After nine cycles, beds of barrier material were found to remove radium from solution.

Soil bacteria, from the Elliot Lake, Ontario, and a river bed of Nova Scotia, under anaerobic conditions reduced sulphate to sulphide. The radium sulphide formed is water soluble increasing the aqueous radium concentration. In the presence of barium arsenate the concentration of radium in the aqueous phase was reduced.

The overhead gas, from the anaerobic cultures were tested for the presence of arsenic, a product expected if the arsenate is reduced. This test was negative, hence it was assumed that the arsenate was not reduced by the microbes in the cultures.

CONTAINMENT OF RADIUM IN TAILING DUMPS AS RADIUM ARSENATE

INTRODUCTION

The first plant to treat uranium ore was built in Czechoslovakia in 1906. It wasn't until 1913 that a second plant was built in Denver, Colorado. In Canada, Eldorado Mining and Refining Limited began working the uranium deposits at Great Bear Lake in 1933. These early operations were primarily concerned with the radium content of the ores.

The uranium industry did not exist in 1940; previous to this time uranium was a by-product of the radium industry. Following World War II the development of nuclear power provided a demand for uranium, hence the expansion of mining and processing of uranium ores.

The mining and milling of uranium ores, by 1982, has produced 133,000,000 tons of uranium tailings at the rate of 25,000 - 30,000 tons daily. Uranium ores contain a number of radionuclides which are inherently dangerous and are associated with the tailings after separation of the uranium from the ore. The primary radioactive contaminants associated with tailings are thorium, radium, radon, lead and polonium.

Wastes, which make up tailings, include wash water, sands, waste solids and various process liquors. These wastes are stored in tailings ponds or lagoons where the volume is reduced by evaporation and seepage of the liquid portion. The composition of tailings in the Elliot Lake area is given in Table 1. These analyses are for the various factions which make up the tailings pond.

TABLE 1

COMPOSITION OF ELLIOT LAKE TAILINGS

	Slimes	Sands
I. Tailings Solids		
Minerals (relative Concentrations		
- Gypsum (%)	10-12	1-4
- Carbonate (%) (Calcite)	0.2	0.005
- Iron (%) ($Fe(OH)_3$)	3	0.5
- Pyrite (FeS_2)	3-7	3-7
Radionuclides		
- RA-226 (pCi/g)	100-500	100-200
- Pb-210 (pCi/g)	100	100
- Po-210 (pCi/g)	50	50
- U (ug/g)	10-100	10-100
- Th (ug/g)	10-300	10-300
II. Pore Water Chemistry		
Radionuclides		
- Ra-226 (pCi/L)	10-300	10-300
- Pb-210 (pCi/L)	5-50	50-5,000
- Po-210 (pCi/L)	--	--
- U (ug/L)	50-200	100-5,000
pH		
- discharge	9-11	9-11
- weathered	3-6	1-5
Other Constituents (mg/L)		
- Al	1-50	1-200
- SiO_2	20-120	20-120
- Ca	400-600	400-600
- Mg	10-250	10-400
- Na	10-40	10-40
- K	10-130	10-170
- SO_4	1,500-10,000	10,000-150,000
- PO_4	0-2	0-2
- Fe	50-5,000	1,000-30,000
- Cu	0-5	0-10
- Zn	5-20	1-50
- Ni	1-5	1-30
- Co	0-4	1-30
- Pb	0-0.5	0-4
- Mn	20-200	0-30

Reference: Beak Consultants Limited, Waste Management Implications of Concentrating Slimes - Characteristics and Potential Problems Report for Atomic Energy Control Board, Ottawa, Canada, May 1986.

During the 1950's and 1960's tailings were deposited as slurries, 30 to 40% solids, in settling ponds for sedimentation of solids without water treatment for the precipitation of radium-226. These settling ponds were constructed by damming low areas in the vicinity of the uranium mill. Radium removal from tailing basin effluents has been common practice since 1965. The treatment consists of adding barium chloride to precipitate barium - radium sulphate which is not completely efficient as it allows suspended radium-226 to be released.

Other means of impounding uranium mine and mill tailings are in use or have been suggested. In Saskatchewan, Gulf uses a pit disposal method in which the pit is an old mine. Key Lake uses a sub-aerial deposition scheme in which the fine tailings cover the coarse tailings. This blanket of fine tailings prevents the water from reaching the coarse tailings underneath as it acts like a clay. This clay material is also effective as a barrier to radon gas.

The disposal of tailings in deep lakes has also been suggested. The lake water would act as a blanket preventing exposure of the material to air preventing oxidation and acidification of the tailings.

It has been shown[1] that the arsenates of barium and radium are more insoluble than their sulphates. Coprecipitation of radium with barium as the arsenates have reduced the concentrations of radium to less than one pCi/L. It has also been demonstrated that radium displaces barium in barium arsenate hence the barium arsenate behaves as an ion exchanger even at low pHs. Using this phenomenon, barium arsenate and ferric arsenate mixed with tailings have been shown to be impervious to radium, i.e. they act as a barrier.

Although the solubility coefficient for $Ba_3(AsO_4)_2$ indicates that it should have a long residence time in the soil, little is known about the effects that biological processes might have on the stability of the compound. Biotransformation of other arsenic compounds have been reported, mediated by both fungi and bacteria[2]. The specific conditions under which these transformations occur have been investigated[3,4,5] but it is difficult to extrapolate from the specific conditions reported, to those which might be anticipated at Elliot Lake. It is likely that temperature, pH, redox potential, presence of nutrients and presence of appropriate microbial populations would interact to affect solubilization of barium arsenate. Each of these factors vary greatly in the Elliot Lake tailings. For example, the pH can range from 2 to 9 depending upon the extent of pyrite oxidation and lime treatment. Similarly, the Eh can vary greatly, particularly if the dissolved oxygen is limiting. Nutrients (as well as pH and Eh) are effected markedly by vegetation cover. Microbial populations can change rapidly in response to altered conditions, propagules being introduced by wind, water or animal activity.

Effluents from base metal, uranium and iron ore mines are subject to controls to limit the discharge of deleterious substances. These controls are expected to provide protection to fish and other aquatic life. Limits have been specified for those parameters which are known to occur commonly in mining effluents in sufficient amounts to be deleterious to fish. The parameters and their limits are summarized in Table 2.

The majority of the uranium mills in Canada use a sulphuric acid leach process to extract the uranium producing acidic residues and acidic liquid wastes. These wastes must be treated prior to discharge of the effluent water to minimize their impact on the environment and meet the guideline limits given in Table 2 for effluent quality. The treatment of acid wastes consists of neutralization with lime to a pH of 8 to 11.5 precipitating the heavy metals. The solid and liquid phases

are separated in a settling pond. The liquid phase is then treated with $BaCl_2$ to precipitate the radium-226 as a barium radium sulphate compound in settling tanks. The resulting water is discharged to the environment. The concentration of radium-226 in the discharge water is usually in the vicinity of 2 to 3 pCi.

TABLE 2

SUMMARY OF ACCEPTABLE EFFLUENT LEVELS AS SET OUT IN REGULATIONS AND GUIDELINES

(For Base Metal, Uranium and Iron Mines)

Parameter	Control Level* (Total Metals)
Lead	0.1 mg/l
Copper	0.3 mg/l
Arsenic	0.5 mg/l
Nickel	0.5 mg/l
Zinc	0.5 mg/l
Total Suspended Matter	25 mg/l
pH	6.0 minimum
Acute Lethality	Not less than 50% survival in a 96-hr acute lethality test (in guidelines only)
Ra 226**	10 pCi/l (dissolved)

* The control level represents a monthly arithmetic mean for the parameter listed.

** For Ra 226 the control level refers to a dissolved analysis using a 3 micron filter.

This study is concerned with the chemistry of radium arsenate to ascertain if by the treatment of uranium mill effluents with arsenate a more stable tailings area will result with a lower concentration of radium-226 in the discharge waters. Tailings, which contain pyrite,

become acidic with time through the production of sulphuric acid by sulphide oxidation hence the variation of radium arsenate precipitation as a function of pH with various coprecipitants is a parameter to know before applying arsenate for the treatment of uranium mill tailings. Furthermore, it is essential to determine the effect of arsenate and pH on the other radionuclides associated with uranium ores, i.e. lead and thorium.

EXPERIMENTAL

Optimization of Barium to Arsenate Ratio

The Elliot Lake tailings were supplied by Energy, Mines and Resources Canada. All other chemicals were from commercial sources. The preparation of solutions and analytical methods are described in the Appendix.

Barriers were prepared and tested in glass columns of 6.5 cm internal diameter and 75 cm in length. Flow rates of effluent were controlled by a stop cock at the lower end. The bottom of the columns consisted of a wad of glass wool covered with 4 cm of silica sand. The barrier layer, 24 cm in height, was added on top of the sand layer and then covered with another wad of glass wool. The glass wood on top of the barrier prevented stirring of the fine tailings on addition of influent.

The barrier material was prepared by mixing 500 g of tailings with 500 g of oil dry. An adsorbent dry product, the oil dry was added to provide a reasonable flow rate of solution through the column. Barium arsenate was added to the tailings - oil dry mixture by mixing 11.2285 g $Na_2HAsO_4 \cdot 7H_20$ and then 4.7040 grams of $BaCl_2 \cdot 2H_20$. The quantity of $Na_2HAsO_4 \cdot 7H_20$ was sufficient to obtain a mixture 1% in ASO_4. The $BaCl_2$ added was sufficient to yield a barium to arsenate molar ratio of 1:2.

Columns were prepared containing barium to arsenate molar ratios of 1:2, 2:2, 3:2, 4:2 and 6:2. A control column was prepared containing only the tailing - oil dry mixture.

The effect of barium to arsenate ratio on the effectiveness of barium arsenate barriers in containing radium in tailings dumps was determined by passing 1 liter of solutions containing 1000 pCi Ra^{226}

through each column. The effluents were collected and analyzed for Ra by measuring the alpha emission. The procedure used for this analysis is given in the Appendix.

Five successive 1 l aliquots containing 1000 pCi Ra/L were passed through the control column and the columns with barium to arsenate ratios of 1:2, 2:2 and 3:2. Columns with barium to arsenate ratios of 4:2 and 6:2 were treated with three successive 1 l aliquots of solution containing 1000 pCi Ra^{226}/L.

After passage of the 1000 pCi Ra^{226}/L solutions through the columns the radium concentration in the influent was increased to 10,000 pCi Ra^{226}/L and the effluents analyzed.

Ageing Effects

Ageing of barriers, i.e. the affect of freeze-thaw and wet-dry cycling on the efficiency of radium containment was determined by passage of a radium solution through a column after the barrier material had completed a cycle. The columns were prepared as for the optimization of the barium to arsenate ratio experiments. The ageing effects were studied at two pH's, 2 and 6, and 1% in $Ba_3(AsO_4)_2$. A control column was carried with these experiments consisting of tailings and oil dry. The effluents were analyzed for radium after each cycle.

Bacteriological Solvation of Radium in Uranium Mill Tailings

The Elliot Lake tailings were supplied by Energy, Mines and Resources Canada. The source of microbes were soils, one from Elliot Lake, supplied by Energy, Mines and Resources and the second a Nova Scotia soil from a river bed.

Sample Preparation

Twenty litres of Elliot Lake tailings were transferred to a 50 litre plastic container and the pH adjusted to 10.5 with sodium hydroxide. The suspension was mixed with the addition of 10,028 pCi of radium - 226. The sample was split into two ten litre samples by transferring 10 L to a second container. 9.1186 grams of $Na_2HAsO_4 \cdot 7H_20$ dissolved in water was mixed with one of the ten litre samples. 10.7016 grams of $BaCl_2 \cdot 2H_20$ in an aqueous solution were added to the sample. The resulting tailings were thus 0.1% in $Ba_3(AsO_4)_2$.

The 10 L of tailings containing $Ba_3(AsO_4)_2$ were split into four aliquots of 2.5 litres and their pH adjusted, one each to pH 2.5, 4.0, 7.0 and 9.0. The other 10 L sample was also split into four fractions and their pH adjusted to 2.5, 4.0, 7.0 and 9.0

The above eight samples were used in testing for the biological solvation of radium in uranium tailings areas. The tests were designed to detect sulphate reduction at pH's from 2.5 to 9.0 with and without $Ba_3(AsO_4)_2$ present, with and without the presence of a carbon source and with and without oxygen. All samples were run in duplicate, with a control inoculum.

The total number of samples was 192, hence each sample was labelled as to the condition and content. Jars with screw caps and rubber seals were used as sample bottles. The caps of the jars were fitted with two puncture seals so they could be regassed during the period of incubation.

Aliquots, 24 of 100 mls, of the pH 2.5 samples were transferred to reaction jars, to half of which was added 1 ml of sugar solution. The samples were then autoclaved for 20 minutes at 121°C and 15 psi pressure. The jars were removed from the autoclave and allowed to cool. The autoclaved samples were then inoculated with the prepared inoculum.

Four samples of the sugar samples were inoculated with the control inoculum, four samples with Elliot Lake inoculum and four samples with Nova Scotia inoculum. Similar samples containing sugar were also prepared with the same inoculum.

Samples at pH's of 4.0, 7.0 and 9.0 were prepared in the same way. Following inoculation the samples were divided. Half were gassed with oxygen and the other half with nitrogen.

The prepared samples were incubated at room temperature for 131 days. During the incubation period the oxygen and nitrogen atmospheres were changed. The gases were transferred from gas cylinders by means of tubing and introduced into the samples by means of hypodermic needles through puncture seals. The overhead gases exited the samples through a second puncture seal and passed through a solution of silver diethyldithiocarbamate. The presence of arsenic in the overhead gas would be detected by the development of color in the silver diethyldithiocarbamate solution.

Inocula Preparation

The control inoculum was prepared by mixing 250 ml of Elliot Lake sediments with water. Two hundred millilitres of the supernatant liquid was mixed with 200 mls of the supernatant prepared from a Nova Scotia sediment. This inoculum was autoclaved.

The Nova Scotia inoculum was prepared by mixing 500 ml of distilled water with the Nova Scotia mud and using the supernatant.

The Elliot Lake inoculum was prepared by mixing Elliot Lake tailings supernatant solution with distilled water and Elliot Lake sediment.

RESULTS AND DISCUSSION

Optimization of Barium to Arsenate Ratio

The data pertaining to optimization of barium to arsenate ratio in barriers to radium is tabulated in Tables 3 and 4. Table 3 contains the analytical results of the effluent analysis which in Run 1 the influent was distilled water and Run 2 the influent was an aqueous solution containing 1000 pCi Ra^{226}/L.

Table 3 illustrates that the variation in ratio of barium to arsenate does not effect the pH of the effluent. The pH remains constant and the same as the pH of solutions passing through the control column which contains no arsenate. The concentration in the effluent of thorium, lead and barium are also kept below the detection limit. Thorium is contained due to the formation of thorium hydroxide which is highly insoluble ($K_{SP} = 4 \times 10^{-45}$) at a pH of 6. Lead and barium are at low concentrations due to the presence of dissolved sulphate as well as arsenate with which both metals form insoluble compounds. The low concentrations of barium and lead are also independent of the ratio of barium to arsenate concentration.

The concentration of ions in the effluents of the control column are independent of the presence of radium in the influent, that is, the concentration of sulphate. Calcium and total solids are essentially the same in Runs 1 and 2.

The radium concentration in effluents from barriers made of Elliot Lake tailings and various ratios of barium to arsenate are presented in Table 4. The effluents were analyzed for radium in every litre. The radium in the effluent of the control column, i.e. no barium arsenate present, showed an increase in radium concentration with each litre of radium passed through, whereas the column containing barium arsenate kept the radium concentration at a low level that is in the 3 pCi Ra/L range. These low levels were obtained with influents containing 1000 and 10,000 pCi Ra/L.

Table 3

Optimization of Ba:AsO_4 Ratio Effluent Analysis

Analysis	1:2	2:2	3:2	4:2	6:2	Control
Run 1						
pH in	5.9	6.0	6.0	6.0	6.0	6.0
pH out	6.4	6.5	6.2	6.2	6.2	6.3
mg SO_4/L	2335	1711	1334	-	-	1238
mg Ca/L	689	855	1000	1333	2105	467
% Total Solids	.69	.74	.74	.93	1.31	.20
mg Th/L	<10	<10	<10	<10	<10	<10
ppm Pb	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
ppm Ba	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
Run 2						
pH in	6.1	6.0	6.1	6.0	6.0	5.9
pH out	6.4	6.2	6.2	6.2	6.2	5.9
mg SO_4/L	1752	1251	1056	923	1328	1373
mg Ca/L	533	453	544	820	1085	464
% Total Solids	.32	.33	.38	.52	.58	.22
mg Th/L	<10	<10	<10	<10	<10	<10
ppm Pb	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
ppm Ba	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25

Table 4

Efficiency of Radium^{226} Removal With Varied Barium to Arsenate Ratios

	Ra^{226} per Effluent Volume in L											
$Ba:AsO_4$	1	2	3	4	5	6	7	8	9	10	11	12
0 : 0	11.6[c]	2.3[a]	5.9	5.4	25.7	45[b]	162		204			337
1 : 2	1.8[c]	<1.6[a]	8.6	3.9	<1.2	1.6[b]	8.2					17.2
2 : 2	2.3[c]	1.8[a]	1.7	<1.2	<1.2	<1.6[b]	1.0					4.4
3 : 2	3.54[c]	<1.6[a]	5.3	4.3	<1.2	1.6[b]	<1.0					2.6
4 : 2	2.6[c]	4.2[a]	1.8					7.2[b]				
6 : 2	2.2[c]	<1.2	<1.0					1.2[b]				

Influent Ra^{226}

(a) 1,000 pCi Ra^{226}/L
(b) 10,000 pCi Ra^{226}/L
(c) 0 pCi Ra^{226}/L

The efficiencies of removal of radium by these barriers were independent of barium to arsenate ratio with influents containing 1000 pCi Ra/L.

Increasing the concentration of radium to 10,000 pCi/L the barriers showed an increase in efficiency as the quantity of barium increased when the concentration of radium was increased to 10,000 pCi/L. The efficiency increased approximately a factor of 10 in going from 1:2 to 3:2 ratio. It is thus apparent that a more reliable barrier is formed with $Ba_3(AsO_4)_2$ than with mixtures containing less barium.

Ageing Effects

Freeze thaw and wet dry cycling have very little effect on the ability of $Ba_3(AsO_4)_2$ to remove radium from solution. The results for the first 5 cycles given in Tables 5 and 6 are for effluents in which the influents contained 100 pCi Ra/L. The latter results are for cycle 9 in which the influent contained 10,000 pCi Ra/L for cycles 6, 7, 8 and 9. It is assumed from these results that weather cycles such as freeze thaw and wet dry are not detrimental to the ability of arsenate to remove radium from solution. The use of barium arsenate as a barrier to the migration of radium from uranium mill tailing dumps is thus applicable in Canadian type weather.

Tables 5 and 6 show that at a pH of 2 the concentration of radium in the effluents is higher than at a pH of 6. This can be attributed to the increase in solubility of radium arsenate with an increase acidity. Table 7 shows that in going from a pH of 6 to 2 the solubility of lead increases. There was a larger increase in the concentration of lead after the wet dry cycle than after the freeze thaw cycle. The indication is that freeze thaw has less effect on the solubility of lead arsenate than does the wet dry cycle.

Table 5

Efficiency of Radium^{226} Removal During Wet Dry Cycling

Column Treatment	pH	Ra^{226} Concentration Per Cycle in l 1	2	3	4	5	6	7	9
1% $Ba_3(AsO_4)_2$	2	21.3[c]	15.0[a]	5.9	24				
1% $Ba_3(AsO_4)_2$	6	<1.6[c]	2.9[a]	4.4	5.3				32[b]
Nil	6	11.6[c]	2.3[a]	5.9	5.4	25.7	45[b]	162	204

Influent Ra^{226}
(a) 1,000 pCi Ra^{226}/l
(b) 10,000 pCi Ra^{226}/l
(c) 0 pCi Ra^{226}/l

NOTE: The pH 2 Wet Dry Cycling had Pb ranging from 6 to 24 ppm in the effluent.

Table 6

Efficiency of Radium^{226} Removal During Freeze Thaw Cycling

Column Treatment	pH	Ra^{226} Concentration Per Cycle in l 1	2	3	4	5	6	7	9
1% $Ba_3(AsO_4)_2$	2	20.6[c]	9.2[a]	11.2	24.4				
1% $Ba_3(AsO_4)_2$	6	<1.6[c]	4.9[a]	1.0	3.2				19.6[b]
Nil	6	11.6[c]	2.3[a]	5.9	5.4	25.7	45[b]	162	204

Influent Ra^{226}
(a) 1,000 pCi Ra^{226}/l
(b) 10,000 pCi Ra^{226}/l
(c) 0 pCi Ra^{226}/l

NOTE: The pH 2 Freeze Thaw Cycling had Pb ranging from 7 to 20 ppm in the effluent.

Table 7

Effect of Ageing Effluent Analysis

Analysis	Wet-Dry	Freeze Thaw	Wet-Dry	Freeze Thaw
Run 1				
pH in	6.0	6.1	2.0	2.0
pH out	6.0	6.3	2.1	2.1
mg SO_4/L	582	776	-	-
mg Ca/L	426	388	1735	1918
% Total Solids	.22	.16	1.58	1.58
mg Th/L	<10	<10	<10	<10
ppm Pb	<1.0	<1.0	24	20
ppm Ba	<1.25	<1.25	<1.25	<1.25
Run 2				
pH in	6.0	6.0	2.0	2.0
pH out	6.2	6.2	2.0	2.1
mg So_4/L	856	529	597	1173
mg Ca/L	384	282	1594	1194
% Total Solids	.22	.15	1.23	1.02
mg Th/L	<10	<10	<10	<10
ppm Pb	<1.0	<1.0	17	9
ppm Ba	<1.25	<1.25	<1.25	<1.25

Biological Solvation of Radium Sulphate

Soil samples collected from the Elliot Lake area and a river bottom in Nova Scotia, were tested for the presence of sulphate reducing microbes. This test consisted of preparing a slurries of Elliot Lake uranium tailings and the solids in water. The formation of sulphide was detected by its familiar odor and the formation of a black precipitate. The formation of sulphide was a result of microbial reduction of the sulphate present in the uranium mill tailings and occurred with both samples of soil.

Bacteriological analysis, Table 8, of the two samples showed both to be inactive at pH's of 2.5 and 4. This inactivity was evident even after 131 days of incubation, Table 9. At pH's of 7 and 9 the soils showed the presence of microbes. The Nova Scotia soil showed 5×10^4 microbes per gram and the Elliot Lake soils showed 58×10^4 microbes/gram at a pH of 7 and 150×10^4 microbes/gram at a pH of 9.

Bacteriological plate counts were also employed to see if growth had occurred in the inoculated tailings sample after incubation for 131 days. The results of this analysis are presented in Table 9 which show, at a pH of 7 and 9, microbe populations of millions per gram. There was an increase in microbe population as the pH increases, that is the microbes are more reactive in the pH of 7 to 9 region than in acid media. Table 9 also indicates that the microbe population increased independent of sugar addition and independent of the presence of oxygen or nitrogen. The microbes failed to grow under all conditions, notably at pH's of 2.5 and 4.0.

The aqueous phases of the incubated tailings - soil mixtures were analyzed for arsenic and barium. The results of these analyses are given in Table 10 and show no correlation with conditions of the media. The lack of correlation is possibly due to the solubility of barium arsenate is independent of the activity of the microbes and the soil samples. The influence of the solubilized radium could not be detected as the radium concentrations involved are 10^6 times smaller than the arsenic and barium.

To maintain aerobic and anaerobic conditions the gaseous phase of the incubating samples were reviewed periodically, ie: the oxygen and nitrogen was changed. During this operation the gas over the samples were transferred by means of rubber tubing to a bubbler containing silver dithiocarbamate solution. The total volume of gas from the incubating samples was 12.8 litres. There was no observable color change of the silver dithiocarbamate solution. This indicates that arsenic formation for the combined samples was less than 1 μg.

The aqueous phase of the incubated samples were analyzed for radium. The results are given in Tables 12, 13, 14 and 15 with the various conditions. The radium values show that the various parameters, with the exception of pH has little effect on the radium released. This is substantiated by the measurement of microbe activity results in Table 9.

A comparison of Table 14 and Table 15 shows that anaerobic conditions yield higher concentrations of dissolved radium in the $Ba_3(AsO_4)_3$ free samples than with the aerobic samples in the pH range of 7 to 9. The corresponding samples containing .1% $Ba_3(AsO_4)_2$ showed considerably less dissolved radium. The tables show that Nova Scotia anaerobes produced more dissolved radium than Elliot Lake anaerobes and vice versa for the aerobes.

The aqueous phases of the bacteriological samples were analyzed for dissolved radium. Table 15 contains the results for those samples in which aerobic conditions were maintained. The concentrations measured for those samples containing barium arsenate are recorded beside their corresponding barium arsenate free samples. In some cases the concentration of radium is given as a less than number. This number varies due to the variation in volume of water available from the samples, hence the aliquot available for radium analysis varied. The range of the lower limit of detection varied from 23 pCi Ra/L with 42 mls sample to 200 pCi Ra/L for a 5 ml sample. Tables 13 and 14 contain

similar results for anaerobic conditions, acid conditions and the control samples respectively.

The control samples were prepared in the same manner as the other biological samples but were autoclaved for twenty minutes at 121°C and 15 psi steam pressure. Autoclaving was employed to kill the microbes. The radium values in Table 10 are similar to the results in Tables 14 and 15 indicating that autoclaving did not kill all the microbes. It is suggested that at least an hour is necessary to kill the microbes. Bacteriological examination of the samples, Table 11, confirmed the presence of microbes in the control samples.

Acidity had a marked effect on the concentration of radium in the aqueous phase. Table 12 shows that, at a pH of 2.5, 5600 to 6400 pCi of radium is present for both the Nova Scotia and Elliot Lake inoculum. The values at pH 4 are at a non detectable level in the absence of barium arsenate. In the presence of barium arsenate at pH's of 2.5 and 4 the radium is high and fairly constant. The values reported for pH 2.5 indicate that barium arsenate has reduced the radium released to the aqueous phase. The results at pH 4 cannot be explained. Microbe activity has not contributed to these values as no microbes were detected at these pH levels, Table 9.

It has been shown that microbes from Elliot Lake, Ontario and Nova Scotia are capable of reducing sulphate in Elliot Lake tailings at pH's of 7 and 9. This reaction occurred in the anaerobic and aerobic samples forming radium sulphide which is water soluble. The reaction occurred in the anaerobic samples at the surface and progressed down through the medium. In the aerobic samples the reaction began beneath the surface of the medium where conditions became anaerobic. The time required for the reaction to be observed in the aerobic samples was about two to three times longer than in the anaerobic samples.

Tables 14 and 15 compare the concentration of radium in the aqueous phase of samples containing barium arsenate with barium arsenate free media. It is quite apparent that the presence of barium arsenate contains the radium in the solid phase over the pH range of 7 to 9. Hence it is expected that radium solubilized by bacteriological activity will be retained by a barrier of barium arsenate.

Table 8

Standard Plate Counts Prior to
Incubation of Samples

Inoculum	pH	microbes/ml
Nova Scotia	2.5	10
Nova Scotia	4.0	170
Nova Scotia	7.0	5×10^4
Nova Scotia	9.0	4×10^4
Elliot Lake	2.5	0
Elliot Lake	4.0	0
Elliot Lake	7.0	58×10^4
Elliot Lake	9.0	150×10^4

Note: These samples were left at room temperature for 20 hours before plates were inoculated.

All aerobic samples
No sugar supplement

Table 9

Standard Plate Counts After 131 Days of Incubation

Inoculum	pH	Microbes/ml: Plates Aerobic	Microbes/ml: Plates Anaerobic	Incubated: 1	2	3	4
Nova Scotia	2.5	0	0	X			
	4.0	0	0	X			
	7.0	18×10^6	28×10^6			X	
	7.0	1.3×10^6	0.8×10^6				X
	7.0	2.4×10^6	2.9×10^6	X			
	7.0	0.6×10^6	0.5×10^6		X		
	9.0	199×10^6	9×10^6			X	
	9.0	1.3×10^6	0.3×10^6				X
	9.0	1.2×10^6	1.3×10^6	X			
	9.0	1×10^6	0.8×10^6		X		
Elliot Lake	2.5	0	0	X			
	4.0	0	0	X			
	7.0	1×10^6	0.6×10^6			X	
	7.0	0.7×10^6	0.1×10^6				X
	7.0	14×10^6	1.5×10^6	X			
	7.0	0.7×10^6	0.1×10^6		X		
	9.0	4.2×10^6	1.5×10^6			X	
	9.0	0.6×10^6	$.05 \times 10^6$				X
	9.0	1.0×10^6	0.5×10^6	X			
	9.0	0.7×10^6	0.2×10^6		X		

Note:
1. With sugar under N_2
2. N_2
3. With sugar under O_2
4. O_2

Table 10

Arsenic and Barium Concentrations in the Aqueous Phase After Incubation

Sample	Treatment 1	2	3	4	pH	ppm As	ppm Ba
1	X				2.5	.38	<2.0
2	X				2.5	.05	<2.0
3	X				2.5	< .05	<2.0
4	X				4.0	< .05	<2.0
5	X				4.0	< .05	<2.0
6	X				4.0	.05	<2.0
7			X		4.0	.10	< .2
8	X				7.0	3.0	4.8
9			X		7.0	.23	2.1
10				X	7.0	.17	2.4
11			X		7.0	1.0	< .2
12				X	7.0	.10	5.1
13	X				7.0	.42	1.6
14		X			7.0	< .06	5.7
15	X				7.0	.30	2.4
16		X			7.0	.28	2.4
17	X				9.0	.08	2.0
18			X		9.0	< .05	2.1
19				X	9.0	.08	1.7
20			X		9.0	.05	1.0
21				X	9.0	.08	2.3
22	X				9.0	.20	1.7
23		X			9.0	.05	3.0
24	X				9.0	.05	1.7
25		X			9.0	.04	4.0

Note: Samples 1,4,7,8,17 are control samples
2,5,9,10,13,14,18,19,22,23 are Nova Scotia Inoculum
3,6,11,12,15,16,20,21,24,25 are Elliot Lake Inoculum

Treatment 1. With sugar under N_2
2. Under N_2
3. With sugar under O_2
4. Under O_2

Table 11

Confirmation of Presence of
Sulphate Reducing Bacteria

Sample	pH	Treatment 1	2	3	4	Inoculum	Sulfate Reducing Bacteria
1	2.5	X				Control	Negative
2	2.5	X				Nova Scotia	"
3	2.5	X				Elliot Lake	"
4	4.0	X				Control	Positive
5	4.0	X				Nova Scotia	"
6	4.0	X				Elliot Lake	"
7	4.0			X		Control	n/a
8	7.0	X				Control	Positive
9	7.0			X		Nova Scotia	"
10	7.0				X	Nova Scotia	"
11	7.0	X				Nova Scotia	"
12	7.0		X			Nova Scotia	"
13	7.0			X		Elliot Lake	"
14	7.0				X	Elliot Lake	"
15	7.0	X				Elliot Lake	"
16	7.0		X			Elliot Lake	"
17	9.0	X				Control	"
18	9.0			X		Nova Scotia	"
19	9.0				X	Nova Scotia	"
20	9.0	X				Nova Scotia	"
21	9.0		X			Nova Scotia	"
22	9.0			X		Elliot Lake	"
23	9.0				X	Elliot Lake	"
24	9.0	X				Elliot Lake	"
25	9.0		X			Elliot Lake	"

Note: Treatment 1. With sugar under N_2
2. Under N_2
3. With sugar under O_2
4. Under O_2

Table 12

Radium Concentrations in Aqueous Phase
of Control Samples

Sample	pH	Untreated Tailings Ra^{226} pCi/L	Treated 1% $Ba_3(AsO_4)_2$ Ra^{226} pCi/L
1	2.5	2242	747
2	4.0	197	600
3	4.0	2725	666
4	7.0	820	332
5	9.0	620	392

Note: Control sample 3 was aerobic - the others anaerobic.
The control for pH 9.0 had a final pH of 7.4.
All samples contained sugar

Table 13

Radium Concentrations Following Anaerobic Incubation at Low pH's

Sample	pH	Untreated Tailings Ra^{226} pCi/L	Treated 1% $Ba_3(AsO_4)_2$ Ra^{226} pCi/L
1	2.5	6482	400
2	2.5	5619	647
3	4.0	<67	744
4	4.0	<67	356

Note: All samples anaerobic containing sugar.
1,3 are Nova Scotia inoculum.
2,4 are Elliot Lake inoculum.

Table 14

Radium Concentrations in Aqueous Phase
Following Anaerobic Incubation

Sample	pH	Untreated Tailings Ra^{226} pCi/L	Treated 1% $Ba_3(AsO_4)_2$ Ra^{226} pCi/L
1	7	1133	<140
2	7	1150	<200
3	9	5176	53
4	9	4673	481
5	7	775	<141
6	7	1026	<200
7	9	1200	341
8	9	860	200

Note: The pH 9.0 samples exhibited pH's close to 7.0 upon completion of incubation.

Samples # 1 - 4 are Nova Scotia Inoculum
5 - 8 are Elliot Lake Inoculum

Samples # 1, 3, 5, 7 contain sugar

Treated with 1% $Ba_3(AsO_4)_2$ only difference - all other conditions are the same.

Table 15

Radium Concentrations in Aqueous Phase
Following Aerobic Incubation

Sample	pH	Untreated Tailings Ra^{226} pCi/L	Treated 1% $Ba_3(AsO_4)_2$* Ra^{226} pCi/L
1	7	1141	<142
2	7	1696	<140
3	9	<100	87
4	9	<92	728
5	7	1889	100
6	7	1010	<144
7	9	440	272
8	9	452	441

Note: The pH 9.0 samples exhibited pH's close to 7.0 upon completion of incubation.

Samples # 1 - 4 are Nova Scotia Inoculum
5 - 8 are Elliot Lake Inoculum

Samples # 1, 3, 5, 7 contain sugar

* Treated with 1% $Ba_3(AsO_4)_2$ - all other conditions are the same.

CONCLUSIONS

Barium arsenate, used as a barrier to the migration of radium in ground waters, is unaffected by wet-dry and freeze-thaw transitions. It is thus applicable for use in Canada as a chemical curtain around existing uranium mill tailing ponds. The use of arsenate as a precipitant of radium in uranium mill streams would also reduce the rate of migration of radium from tailing ponds into the surrounding waters.

Variations in the ratio of barium to arsenate in radium barriers has little effect on efficiency of these barriers for aqueous phases containing less than one thousand picocuries per litre of radium-226. At concentrations of ten thousand picocuries of radium per litre the efficiency increases as the ratio of barium to arsenate increases. The highest efficiency is obtained with barium to arsenate ratio of two to three, i.e. with the compound $Ba_3(AsO_4)_2$.

Biological activity can reduce the sulphate in uranium mill tailings to sulphides. The reduction converts radium sulphate,m an insoluble compounds, to soluble radium sulphide, hence, the radium is free to migrate in the ground waters. The microbes responsible for the reduction of sulphate are active in alkaline medium with highest activity at a pH of 7.4. There was no evidence that arsenate was reduced by means of microbes.

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APPENDIX

REAGENTS

1) Lead nitrate solutions: 1.2790 g $Pb(NO_3)_2$/2 L, 400 ppm Pb
   12.79 g $Pb(NO_3)_2$/L, (Ra^{226})

2) Citric acid solution: 192.13 g $C_6H_8O_7$/L, 1M

3) Barium nitrate solution: 0.19032 g $Ba(NO_3)_2$/L, 0.1 mg/ml Ba

4) EDTA, disodium salt, solutions: 93.05 g/L, 0.25 M
   37.22 g/L, 0.10 M
   3.723 g/L, 0.01 M

5) Ammonium sulfate solution: 100 g $(NH_4)_2SO_4$/L

6) Arsenious Oxide Standard Solutions:

   A stock solution was prepared by dissolving 1.320 g As_2O_3 in 25 ml of 20% NaOH in a 1 L volumetric flask and diluted to the mark with distilled H_2O.

   A 10 ugAs/ml solution was prepared by taking 10 ml of stock solution and diluting to 1 L in a volumetric flask .

   A 1 ugAs/ml solution was prepared by diluting 50 ml of the 10 ugAs/ml solution to 500 ml in a volumetric flask.

7) Dilute HCl: dilute 144 ml conc HCl to 200 ml with DH_2O

8) Hydrochloric acid: HCl 12 M, 0.1 M

9) Ammonium hydroxide: NH_4OH 14.3 M

10) Sulfuric acid: H_2SO_4 8 M

11) Acetic acid: CH_3COOH 17.4 M

12) Nitric acid: HNO_3 5 M

13) Sodium Hydroxide: NaOH 10 M
    NaOH 1 M
    NaOH 0.1 M

14) Pyridine

15) Methyl red indicator

16) Alizarin red S indicator

17) Phenolphthalien indicator

18) Murexide (ammonium purpurate): 200 mg per 100 g
Solid NaCl
Ground to 40 - 50
Mesh

19) Radium -226

A standard stock solution of Ra -226 was prepared by diluting a certified solution of 6.47 μCi of Ra -226 in 5 mls of 0.5 M HCI to 2.0 litres. The stock solution contained 16,175 pCi of Ra -226 per millilitre. Radium solutions of required concentrations were made by dilution of measured volumes of the stock solution.

20) Thorium Nitrate, 400 ppm Th

Thorium nitrate solution was prepared by dissolving 0.952 g of $Th(NO_3)_4 \cdot 4\ H_2O$ in distilled water and diluting to the mark in a 1 L volumetric flask.

21) Stannous chloride solution: 40 g $SnCl_2$/100 ml HCl
40% in HCl

22) Lead acetate solution: 10 g $Pb(CH_3COO)_2 \cdot 3\ H_2O$
per 100 mls H_2O
10% in H_2O

23) Potassium Iodide solution: 15 g KI/100 ml H_2O
15% in H_2O

24) Silverdiethydithiocarbamate solution: 0.5 g in 100 mls
pyridine

25) Barium chloride solution: 100 g $BaCl_2 \cdot 2\ H_2O$/L H_2O

26) Silver nitrate - nitric acid reagent: 8.5 g $AgNO_3$ in 0.5 ml conc
HNO_3 in 500 ml H_2O

27) Ammonium chloride - ammonium hydroxide buffer

16.9 g NH_4Cl
143 ml conc NH_4OH
1.179 g disodium salt EDTA dihydrate
780 mg $MgSO_4 \cdot 7\ H_2O$

EDTA and $MgSO_4 \cdot 7\ H_2O$ were dissolved in 50 ml H_2O and mixed with a second solution of NH_4Cl and 143 ml of NH_4OH in a 250 ml volumetric flask. The resulting solution was diluted to the mark.

28) Dilution media 1% peptone in distilled water.

29) Carbon source for biological solubilization of barium arsenate

10 g glucose
10 g yeast extract
10 g sodium acetate

Dissolved in 100 ml of distilled water.

One ml of this solution was added by syringe to each sample requiring a carbon source.

CHEMICAL METHODS

a) Determination of Thorium

Pipet 25 mls of sample into a 500 ml Ehrlenmeyer flask and dilute to 200 mls. Add 4 drops of Alizarin Red S indicator and adjust pH to 2.5 with ammonium hydroxide or nitric acid. Titrate solution with 0.025 M versene until pink in color begins to fade rapidly. Adjust the pH to 3.0 and continue titration. The end point is indicated when the pink color disappears giving a clear yellow color.

Calculation

$$\text{mg of Th/L} = \frac{232.1 \times V \times M}{\text{Sample Volume}} \times 1000$$

V = Volume of versene solution

M = Molarity of versene solution.

b) Determination of Lead and Barium by Atomic Absorption Spectrophotometry

Instrument

Perkin Elmer Model 560, Atomic Absorption Spectrophotometer

Lead

Conditions Air-Acetylene
283.3 nm

To 10 ml aliquots of solution was added 1 ml of concentrated nitric acid in a 50 ml volumetric flask. The absorption obtained in the atomic absorption instrument was compared with the absorption of standard solutions and the metal iron concentration calculated.

Barium

Conditions Acetylene - N_2O
553.6 nm

To 10 ml aliquot of sample was added 1 ml of HCl and 0.02 g of KCL. The absorption obtained was compared with standard solutions and the concentration calculated.

c) pH

pH's were measured by a pH meter.

Instrument

Corning Scientific Instruments
pH meter, Model 7

d) Arsenic Method

Water Samples

A 10 ml aliquot of sample was placed in the generation flask and 7 ml of 1:1 H_2SO_4 added. The volume was adjusted to 50 ml with distilled water. To the generation flask was added 5 ml of dilute HCl, 5 mls KI and 10 drops of $SnCl_2$. The solutions were allowed to stand at least 15 minutes to reduce arsenate to arsenite.

Lead acetate impregnated cotton was inserted into the glass tube and 7 ml of sodium diethyldithiocarbamate reagent were measured into the receiving tube.

Four grams of zinc metal were added to the solution and the apparatus connected to trap arsine gas. The sample generated for 30 minutes, was disconnected and silver diethyldithiocarbamate reagent mixed with an air jet and poured into a cell.

Standards were prepared and analyzed with the samples at 535 nm on the spectrophotometer. A standard curve was plotted and the amount of As present in the samples calculated using the curve.

e) Calcium Method

Calcium was determined using an EDTA titrimetric method.

A 5 ml aliquot was diluted to 50 ml with distilled water in a beaker. To this was added 2.0 ml of 1N NaOH bringing the pH up to 12 - 13, 0.2 g of murexicle indicator was added and the solution titrated immediately with standardized 0.01 M EDTA to the purple end point.

Calculation:

$$\text{mg Ca/L} = \frac{\text{A x B x 400.8}}{\text{ml Sample}}$$

A = ml titrant for sample

B = mg $CaCO_3$ equivalent to 1 ml EDTA titrant at the calcium indicator end point.

g) Radium^{226} Method

An aliquot of sample was pipetted into a 600 ml beaker. The volume was adjusted to 300 ml with distilled water. The solution was heated to boiling on a hot plate with stirring and then 20 ml of 1 M citric acid solution added. Using pH paper, the pH was adjusted to 8-9 with concentrated ammonium hydroxide and 10 ml of lead nitrate, 3 ml of barium nitrate and 5 ml of $(NH_4)_2SO_4$ added.

Using a pH meter, the pH of the solution was adjusted to 0.9-1.0 with 8 M sulfuric acid.

The sample was stirred for an hour and then filtered using black 47 mm, 0.45 μm Sartorius cellulose nitrate filter. The magnetic stirrer was left in the beaker and the filtrate discarded.

The filter was transferred back to the beaker and the precipitate washed from the filter with distilled water.

The volume was adjusted to 200 mls with distilled water and concentrated ammonium hydroxide added to adjust the pH to 8-9, and 7 ml of 0.25 M EDTA and 5 ml of ammonium sulfate added. The solution was heated to nearly boiling and the precipitate dissolved.

The black filter was removed from the beaker and the pH adjusted to 4.8 with glacial acetic acid. The solution was stirred for an hour and filtered on another 47 mm, 0.45 μm cellulose nitrate filter.

The filter was placed on an aluminum planchette, air dried and radium determined with an alpha spectrometer on a Canberra Multi Channel Analyzer (Series 20) using a solid state 300 mm^2 surface barrier detector.

Standards were prepared by the same method and a standard curve prepared.

The radium 226 concentrations of the samples were calculated using the standard curve.

Instrument

Canberra Series 20 Multi Channel Analyzer

AMP	SCA	ADC
Gain 160.00	LLD 0%	Gain 1024
Input Pos	ULD 110%	PHA ADD
Shaping Slow		Offset 0
		Zero 0

h) Total Solids Method

The column effluent water samples were stirred and 100 ml aliquot pipetted into pre dried, pre weighed 150 ml beakers.

The samples were evaporated to dryness and heated to a constant weight at 100°C.

i) Carbonate Analysis Method

Carbonate was determined by titration with 0.1N HCl (standardized). Pre boiled and cooled water was used throughout this analysis. A one gram sample of tailings was weighed and added to 100 mls pre boiled, cooled H_2O. The sample was stirred for 5 minutes and titrated with 0.1N HCl to methyl red end point and 5 ml excess added. The solution was then boiled for approximately 3 minutes, cooled and the excess acid titrated with standardized 0.1N sodium hydroxide solution.

Calculation

$$2\ HCl + CO_3^{=} \rightarrow H_2CO_3$$

$$\% CaCO_3 = \frac{(V_1N_1 - V_2N_2)\ (.050035)\ (100)}{W}$$

V_1 = Volume of HCl used in ml
N_1 = Normality of HCl
V_2 = Volume of NaOH in ml
N_2 = Normality of NaOH
W = Sample weight in g
.050035 is equivalent weight factor (eg: $CaCO_3$/ml)

j) Sulfate Method

A gravimetric sulfate determination was used. The sulfate was precipitated from a boiling acidic (HCl) solution using $BaCl_2$.

Water soluble sulfate and total sulfate were done by this method.

A one gram sample of tailings was weighed for hot water soluble sulfate.

To the sample 100 mls distilled water was added and the sample boiled for 5 minutes to release water soluble sulfate.

The sample was then filtered through a Whatman # 40 filter paper and washed with hot water.

The volume was adjusted to 200 mls and the sulfate precipitated.

Gravimetric Procedure

The sample volume was adjusted to 250 ml with distilled water. The pH was adjusted to 4.5 - 5.0 with HCl using methyl red indicator. An excess of 1-2 ml HCl was added.

The solutions were heated to boiling, and warm $BaCl_2$ solution was added slowly with stirring until precipitation appeared completed. Two mls $BaCl_2$ was added in excess. The precipitate was digested at 80° to 90° overnight.

The sample was filtered at room temperature through Whatman # 42 ashless filter paper and the precipitate washed with warm distilled H_20 until filtrate is free of chloride ions as indicated by $AgNO_3$-nitric acid reagent.

The filter was charred on a hot plate and then ignited at 800°C for 1 hour in pre weighed porcelain crucibles, cooled in a desiccator and weighed.

Calculation

$$\text{mg } SO_4/L = \frac{\text{mg } BaSO_4 \times 411.6}{\text{ml sample}}$$

BACTERIOLOGICAL METHODS

a) Plate Counts

Prepared Standard Methods agar was sterilized at 121°C and 15 pSi, cooled and poured into the plates in a laminar flow hood.

The anaerobic plates were prepared the same way with the addition of cysteine HCl, .125 g/500 ml agar to make the media reducing. The anaerobic plates were stored under N_2 until inoculated.

The biological solubilization of barium arsenate samples were opened in the larminar flow hood, mixed well and a 1 ml aliquot transferred to the dilution tube. The dilution tubes contained 9 ml of 1% peptone.

The dilution series was prepared 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and four of the dilutions, a 0.1 ml volume were streaked on plates using a plate spreader 10^{-1}, 10^{-3}, 10^{-4}, 10^{-5}. They were streaked on both aerobic and anaerobic plates.

The plates were incubated at room temperature for 72 hours and counted.

b) Sulfate Reducing Bacteria

A Lactate Medium, specific for sulfate reducers was prepared according to:

Yeast Extract	1.0 g
Sodium Lactate	4.0 g
Ammonium Chloride	0.5 g
Potassium Hydrogen Phosphate	1.0 g
Magnesium Sulfate Hepta Hydrate	0.2 g
Calcium Chloride Dihydrate	0.1 g
Iron Sulfate Hepta Hydrate	0.1 g
Sodium Sulfate	0.5 g

The media was mixed with 1 L of distilled water and sterilized at 121°C for 15 minutes.

A 0.5 ml aliquot of the sample was pipetted into pre labeled, pre sterilized test tubes. The test tube was filled with media and closed with a screw cap. The samples were incubated at room temperature and checked periodically for the formation of a black iron sulfide precipitate around the cultures.

The samples that turned black were considered positive.

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